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(54) **Electrically conductive paste and glass substrate having a circuit thereon**

Elektrisch leitende Paste und Glassubstrat mit aufgetragenem elektrischen Schaltkreis

Pâte électriquement conductrice et substrat en verre ayant un circuit électrique déposé sur celui-ci

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to an electrically conductive paste for forming an electrode or a circuit on a substrate such as a glass substrate, and more particularly, to an electrically conductive paste which is applied and baked to form an electrode to which an object is soldered by use of a solder containing no lead (hereinafter referred to as "lead-free solder"). The invention also relates to a glass substrate having a circuit thereon suitable for producing, for example, an automobile window having an antifogging property.

Background Art

[0002] Conventionally, an Sn/Pb eutectic solder has been widely used for soldering a conductor such as a lead terminal to a thick film electrode which is formed by applying and baking an electrically conductive paste.

[0003] In recent years, concern about the environment has increased, and a material containing no toxic lead, i.e., a lead-free solder, has been gradually replacing a conventionally employed solder for connecting a lead terminal. Typically, there is widely employed a lead-free solder comprising Sn as a primary component and at least one metal selected from a group consisting of Bi, Ag, Zn, In, and Sb.

[0004] However, when electric connection of a conductor such as a lead terminal is to be established by use of a lead-free solder, heat resistance, and wettability of the conductor with respect to a solder are insufficient, resulting in poor reliability in terms of electric connection. This problem is partly due to the presence of lead borosilicate glass frit contained in an electrically conductive paste which is used so as to enable the paste to be fired at a low temperature that allows use of a glass substrate.

[0005] In addition, regarding the glass frit that constitutes an electrically conductive paste, the glass frit itself, like a solder, is desirably employed as a lead-free material, in consideration of the environment.

[0006] Electrically conductive paste comprising an electrically conductive component and a B-Bi-O glass frit is known from JP 10012043 A.

[0007] S. P. Yawale et al.: "D.c. conductivity and hopping mechanism in Bi_2O_3-B_2O_3 glasses", Journal of Materials Science, GB, Chapman & Hall Ltd. London, Vol. 28, No. 20, pages 5451 to 5455 disclose an electrically conductive glass frit.

[0008] An electrically conductive paste for use with a ceramic substrate and comprising B-Si-Bi-O is known from JP 09180541 A. An electrically conductive paste having the features of the preamble of claim 1 is known from JP 09092028 A.

SUMMARY OF THE INVENTION

[0009] To overcome the above described problems, preferred embodiments of the present invention provide an electrically conductive paste which contains no lead, which can be fired at low temperature, and which has excellent heat resistance and wettability with respect to a lead-free solder. The preferred embodiments of the present invention also provide a glass substrate having a circuit thereon used for an automobile window having an anti fogging property for example.

[0010] The present inventors have conducted extensive studies and experiments to attain the above objects, and in particular have constructed an electrode through application and baking an electrically conductive paste, and investigated the relationship between the species of the glass frit, and heat resistance of the resultant electrode against a solder or wettability of the solder with respect to the electrode in the case in which the electrode is soldered with a lead-free solder such as an Sn-Ag-Bi solder or Sn-Ag-Cu solder. As a result, the inventors have found that use of a B-Si-Bi-O glass frit provides excellent heat resistance, and wettability with respect to the solder. The present invention has been accomplished based on this finding.

[0011] The above object is achieved with an electrically conductive paste having the features of claim 1. Subclaims are directed to preferable embodiments.

[0012] By employment of B-Si-Bi-O glass frit, heat resistance, and wettability with respect to solder of an electrode formed by applying and baking an electrically conductive paste containing the frit can be enhanced during soldering by use of a lead-free solder.

[0013] By employment of a glass frit having the inventive composition, heat resistance, and wettability with respect to solder of an electrode formed by applying and baking an electrically conductive paste containing the frit can assuredly be enhanced during soldering by use of a lead-free solder.

[0014] By addition of Ni or CuO, the electrical resistance of the paste is controlled to thereby obtain an electrically conductive paste having a desired characteristic, making the present invention even more useful.

[0015] In the electrically conductive paste according to the invention, the glass frit more preferably comprises B_2O_3 in an amount of 10.0-29.0 mol%, SiO_2 in an amount of 10.0 mol% or less (excluding 0 mol%), and Bi_2O_3 in an amount of 71.0-90.0 mol%.

[0016] By employment of a glass frit having the above more preferred composition, heat resistance, and wettability with respect to solder of an electrode formed by applying and baking an electrically conductive paste containing the frit can be enhanced during soldering by use of a lead-free solder.

[0017] Preferably, in the electrically conductive paste containing an electrically conductive component, the component predominantly comprises (a) Ag or (b) a combination of Ag and at least one metal selected from a group consisting of Cu, Pd, and Pt.

[0018] By employment of such an electrically conductive component, there can be obtained an electrically conductive paste which can assuredly form an electrode having sufficient electric conductivity.

[0019] In a second aspect of the present invention, the above described electrically conductive paste is used to form an electric conductor by baking thereof, and soldering by a lead-free solder is performed to the electric conductor.

[0020] By the above electric conductor, sufficient wettability of the electrode with respect to the solder can be provided.

[0021] Thus, an electrode or a conductor can be formed on a substrate such as a glass substrate by use of an electrically conductive paste containing lead-free glass frit, and an electric conductor such as a lead terminal can assuredly be connected to the electrode or conductor by use of a lead-free solder.

[0022] In a third aspect of the present invention, there is provided a glass substrate having a circuit thereon, wherein the circuit is formed through application of the electrically conductive paste on a glass substrate, and baking.

[0023] The glass substrate having a circuit thereon exhibits excellent bonding strength between the glass substrate and the circuit and sufficient reliability.

[0024] In a fourth aspect of the present invention, there is provided a method for producing an automobile window having an antifogging property comprising the steps of applying the electrically conductive paste on a glass substrate and baking.

[0025] The method can provide anti-fogging glass which is useful as an automobile window and which has excellent properties, including enhanced adhesion between the circuit and the glass substrate, high quality, and high reliability.

BRIEF DESCRIPTION OF THE DRAWING

[0026] Various other objects, features, and many of the attendant advantages of the present invention will be readily appreciated as the same becomes better understood with reference to the following detailed description of the preferred embodiments when considered in connection with an accompanying drawing, in which:

FIG. 1 is a ternary compositional diagram of glass frit samples in Examples of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0027] Various modes of the present invention will next be described in detail by way of examples so as to facilitate understanding of features of the invention.

Production of glass frit

[0028] Glass frit samples were produced by the following procedure.

[0029] Starting materials H_3BO_3, SiO_2, Bi_2O_3, and Pb_3O_4 (Pb_3O_4 was used only for Sample No. 1) were mixed so as to attain the compositional proportions shown in Table 1. Each of the resultant mixtures was placed in an alumina crucible, fused at 1200°C, and cooled immediately for vitrification.

[0030] The resultant glass was crushed with zirconia balls or like means, to thereby obtain glass frit.

Table 1

Sample No.	Composition of glass frit			
	B_2O_3	SiO_2	Bi_2O_3	PbO
*1	17	39	12	32
2	10	0	90	0

Table 1 (continued)

Sample No.	Composition of glass frit			
	B_2O_3	SiO_2	Bi_2O_3	PbO
3	19	0	81	0
4	10	10	80	0
5	19	10	71	0
6	25	11	64	0
7	40	0	60	0
8	10	30	60	0
9	40	10	50	0
10	21	30	49	0
11	60	0	40	0
12	10	50	40	0
*13	5	2	93	0
*14	5	45	50	0
*15	71	1	28	0
*16	47	28	25	0
*17	7	61	32	1
<Samples marked with asterisk (*) fall outside the scope of the present invention>				

[0031] Glass frit (3 wt.%), Ag powder (76 wt.%), Ni powder (1 wt.%), CuO powder (1 wt.%), and an organic vehicle (19 wt.%) were mixed, then kneaded and dispersed with a three-roll kneader, to thereby produce an electrically conductive paste. A cellulose resin (8 wt%) dissolved in terpineol was used as the organic vehicle.

[0032] In this step, Ni powder and CuO powder were added so as to adjust the electrical resistance.

[0033] The electrically conductive paste produced in the manner described above was applied, by way of printing, to a surface of a slide glass substrate (square-shaped soda-lime glass plate; 7.0 mm × 7.0 mm × 0.4 mm thickness) so as to form a square shape (6 mm × 6 mm). The glass plate bearing the paste was dried at 150°C for 10 minutes, and baked at 640°C for 1 minute (in-out 5 minutes), to thereby form an electrode.

Evaluation of soldering characteristics

[0034] The solderability of the electrode was evaluated through a meniscograph method.

[0035] In the meniscograph method, a thick electrode film is dipped in a solder bath or a solder bowl, and the buoyancy of the sample is measured to thereby evaluate the heat resistance, and wettability of the electrode with respect to the solder.

[0036] Specifically, the relation force (wetting force; y-axis) versus time (x-axis) is plotted. The time elapsed before balance between buoyancy and tension is achieved following wetting of the thick electrode film (that is, the time elapsed before the curve crosses the x-axis) is called zero cross time (T0). Also, the time elapsed before the thick electrode film has begun to be "bitten" by the solder and the tension has begun to decrease (that is, the time at which the curve begins to slope downward toward the x-axis) is called "solder biting" start time (T1). The shorter the zero cross time (T0), the more excellent the wettability. The longer the "solder biting" start time (T1), the more excellent the heat resistance.

[0037] The results of the solderability test of each sample as measured with respect to an Sn-Ag-Bi solder are shown in Table 2, and those with respect to an Sn-Ag-Cu solder are shown in Table 3. In Tables 2 and 3, the data of Sample No. 1-a represent the results of solderability measurement using a Pb-Sn solder.

Table 2

Sample No.	Wettability (250°C) (Solder: Sn-Ag-Bi)	Heat resistance (290°C) (Solder: Sn-Ag-Bi)
	T0 (s)	T1 (s)
*1-a	1.5	4.8
*1	3.5	3.5
2	0.8	5.0
3	1.0	6.5
4	1.2	6.7
5	1.1	6.3
6	1.4	5.7
7	1.3	5.1
8	1.9	4.7
9	1.5	5.8
10	2.5	5.5
11	2.0	4.9
12	2.8	5.1
*13	1.5	3.8
*14	3.5	4.1
*15	3.0	3.1
*16	4.0	3.5
*17	3.7	3.6

<Samples marked with asterisk (*) fall outside the scope of the present invention>
<*1-a: Results of evaluation when Sn-Pb solder was used>

Table 3

Sample No.	Wettability (250°C) (Solder: Sn-Ag-Cu)	Heat resistance (290°C) (Solder: Sn-Ag-Cu)
	T0 (s)	T1 (s)
*1-a	1.5	4.8
*1	3.2	3.8
2	1.1	5.2
3	0.8	6.2
4	1.0	6.6
5	1.1	6.0
6	1.5	5.9
7	1.4	5.3
8	2.0	5.0
9	1.6	5.5
10	2.4	5.5

<Samples marked with asterisk (*) fall outside the scope of the present invention>
<*1-a: Results of evaluation when Sn-Pb solder was used>

Table 3 (continued)

Sample No.	Wettability (250°C) (Solder: Sn-Ag-Cu)	Heat resistance (290°C) (Solder: Sn-Ag-Cu)
	T0 (s)	T1 (s)
11	1.9	4.9
12	2.9	5.8
*13	1.9	3.5
*14	3.5	4.5
*15	2.8	3.1
*16	3.7	3.5
*17	3.5	3.4

[0038] In Tables 2 and 3, Sample Nos. marked with asterisk (*) are comparative examples, which fall outside the scope of the present invention.

[0039] The composition of glass frit of each sample is shown in FIG. 1. In FIG. 1, black solid square marks labeled with numerals 2 to 12 represent samples which fall within the scope of the present invention, and white square marks labeled with numerals 13 to 17 represent samples of comparative examples.

[0040] As shown in Tables 2 and 3, samples in which electrodes are formed through use of an electrically conductive paste of the present invention exhibit enhanced wettability and enhanced heat resistance as compared with a conventional product (Comparative Example; i.e., Sample No. 1) using Pb glass frit.

[0041] Also, it was confirmed that an electrode formed of an electrically conductive paste having a composition falling within the scope of the present invention are equivalent or superior to conventional products in terms of specific resistivity, bonding strength, and so forth, although these results are not shown in Tables 2 and 3.

[0042] In the above modes of the invention, Ag powder was used as an electrically conductive component. However, a metal powder which contains at least one metal selected from a group consisting of Ag, Cu, Pd, and Pt can also be used as an electrically conductive component.

[0043] When a circuit is formed on a glass substrate through use of an electrically conductive paste of the present invention, it is possible to obtain antifogging glass useful for an automobile window which realizes high bonding strength with an electrode and enhanced reliability. Descriptions of the production method and specific structure of such an antifogging glass for an automobile window are omitted, as the same do not particularly differ from known ones.

Claims

1. An electrically conductive paste comprising an electrically conductive component and a B-Bi-O glass frit, optionally including silicium the glass matrix
characterized by
further containing Ni powder or CuO powder so as to adjust electrical resistance of the paste,
the glass frit being lead-free and comprising B_2O_3 in an amount of 10.0-60.0 mol%, SiO_2 in an amount of 50.0 mol% or less, and Bi_2O_3 in an amount of 40.0-90.0 mol%.

2. An electrically conductive paste according to claim 1, **characterized in that** the glass frit comprises B_2O_3 in an amount of 10.0-29.0 mol%, SiO_2 in an amount of 10.0 mol% or less (excluding 0 mol%), and Bi_2O_3 in an amount of 71.0-90.0 mol%.

3. An electrically conductive paste according to any one of claims 1 or 2, **characterized in that** the electrically conductive component predominantly comprises

   (a) Ag, or
   (b) a combination of Ag and at least one metal selected from a group consisting of Cu, Pd, and Pt.

4. An electrically conductive paste according to any one of claims 1 through 3, **characterized in that** the electrically conductive paste is used to form an electric conductor by baking thereof, and soldering by a lead-free solder is performed to the electric conductor.

5. A glass substrate having a circuit thereon, wherein the circuit is formed through application of the electrically conductive paste as described in any one of claims 1 through 4 on a glass substrate, and baking.

6. An automobile window having an antifogging property comprising the glass substrate having a circuit thereon as described in claim 5.

Revendications

1. Pâte électriquement conductrice comprenant un composant électriquement conducteur et une fritte de verre de B-BI-O, comportant facultativement de la silice dans la matrice de verre,
caractérisée en ce que :

elle contient en outre de la poudre de Ni ou de la poudre de CuO afin d'ajuster la résistance électrique de la pâte, la fritte de verre étant dépourvue de plomb et comprenant B_2O_3 en une quantité de 10,0 à 60,0 mol%, SiO_2 en une quantité de 50,0 mol% ou moins, et Bi_2O_3 en une quantité de 40,0 à 90,0 mol%.

2. Pâte électriquement conductrice selon la revendication 1, **caractérisée en ce que** la fritte de verre contient B_2O_3 en une quantité de 10,0 à 29,0 mol%, SiO_2 en une quantité de 10,0 mol% ou moins (à l'exclusion de 0 mol%), et Bi_2O_3 en une quantité de 71,0 à 90,0 mol%.

3. Pâte électriquement conductrice selon l'une quelconque des revendications 1 et 2, **caractérisée en ce que** le composant électriquement conducteur comprend de façon prédominante :

(a) Ag, ou bien
(b) une combinaison de Ag et d'au moins un métal choisi dans le groupe comprenant Cu, Pd et Pt.

4. Pâte électriquement conductrice selon l'une quelconque des revendications 1 à 3, **caractérisée en ce que** la pâte électriquement conductrice est utilisée pour former un conducteur électrique par cuisson de celle-ci, et un soudage au moyen d'une soudure dépourvue de plomb est effectué avec le conducteur électrique.

5. Substrat de verre portant un circuit, où le circuit est formé par application d'une pâte électriquement conductrice telle que définie dans l'une quelconque des revendications 1 à 4 sur un substrat de verre, et cuisson.

6. Vitre d'automobile possédant des propriétés antibrouillard, qui comprend le substrat de verre portant un circuit comme décrit dans la revendication 5.

Patentansprüche

1. Elektrisch leitende Paste, die einen elektrisch leitenden Bestandteil und eine B-Bi-O-Glasfritte umfasst, die optional Silika in der Glasmatrix einschließt,
gekennzeichnet durch
außerdem Ni-Pulver bzw. CuO-Pulver enthaltend, um den elektrischen Widerstand der Paste einzustellen, die Glasfritte, die bleifrei ist und B_2O_3 in einer Menge von 10,0 - 60,0 Mol.%, SiO_2 in einer Menge von 50,0 Mol. % oder weniger, und Bi_2O_3 in einer Menge von 40,0 - 90,0 Mol.% umfasst.

2. Elektrisch leitende Paste nach Anspruch 1, **dadurch gekennzeichnet, dass** die Glasfritte B_2O_3 in einer Menge von 10,0 - 29,0 Mol.%, SiO_2 in einer Menge von 10,0 Mol.% oder weniger (ausgenommen 0 Mol.%) und Bi_2O_3 in einer Menge von 71,0 - 90,0 Mol.% umfasst.

3. Elektrisch leitende Paste nach einem der Ansprüche 1 oder 2, **dadurch gekennzeichnet, dass** der elektrisch leitende Bestandteil überwiegend umfasst

(a) Ag oder

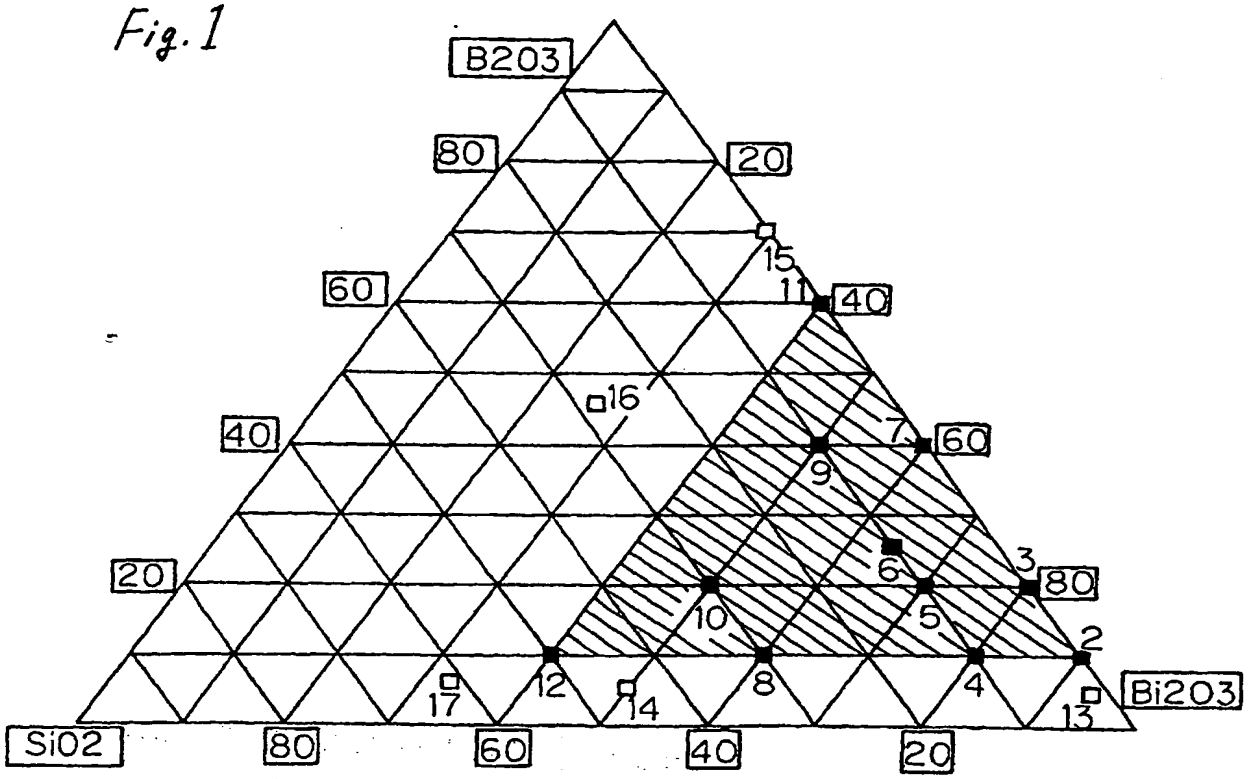
(b) eine Kombination von Ag und mindestens eines Metalls, das aus einer Gruppe ausgewählt ist, die aus Cu, Pd und Pt besteht.

4. Elektrisch leitende Paste nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, dass** die elektrisch leitende Paste verwendet wird, um einen elektrischen Leiter durch deren Härten herzustellen, und das Löten mit einem bleifreien Lot an dem elektrischen Leiter durchgeführt wird.

5. Glassubstrat, das eine Schaltung darauf aufweist, worin die Schaltung über das Aufbringen der elektrisch leitenden Paste, wie in einem der Ansprüche 1 bis 4 beschrieben, auf einem Glassubstrat und das Härten hergestellt ist.

6. Autoscheibe, die eine beschlagverhütende Eigenschaft aufweist, die das Glassubstrat umfasst, das eine Schaltung darauf aufweist, wie in Anspruch 5 beschrieben.

Fig. 1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